Supporting information

Visible-Light Mediated Synthesis of Main-Chain-Type Semifluorinated Alternating Terpolymers by NaI Catalyzed START Polymerization

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Table of contents

S1 Synthesis of monomers

Synthesis of α, ω-unconjugated dienes[1,2]

Synthesis of 1,4-diprop-2-enoxybenzene (B2-1). Under an inert atmosphere, a mixture of hydroquinone (5.0 g, 45.5 mmol), allyl bromide (16.5 g, 136.5 mmol), anhydrous potassium carbonate (12.5 g, 91.0 mmol), and dried acetone (100 mL) were added to a 250 mL three-necked round flask, which was refluxed for 12 h and cooled to room temperature. After removing the potassium carbonate by filtration, the solvent was removed by rotary evaporation. The crude solid product was dissolved in ethyl acetate (150 mL) and then washed three times with 50 mL of deionized water to collect the organic layer. Then the organic layer was dried over sodium sulfate and filtered to remove the sodium sulfate. The solvent was evaporated, and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to obtain a white solid (7.86 g, 41.4 mmol, 91.0%). ^{1}H NMR spectrum of B2-1 was shown in **Figure S1**. ^{1}H NMR (CDCl$_3$, 300 MHz), δ ppm: 6.85 (s, 4H), 6.11-5.98 (m, 2H), 5.43-5.24 (m, 4H), 4.50-4.47 (d, 4H).

Synthesis of 1,4-bis (but-3-en-1-yloxy) benzene (B2-2). Under an inert atmosphere, a mixture of hydroquinone (1.1 g, 10.0 mmol), 4-bromo-1-butene (3.38 g, 25.0 mmol), anhydrous potassium carbonate (6.21 g, 45.0 mmol), and dried acetonitrile (100 mL) were added to a 250 mL three-necked round flask, which was refluxed for 36 h and cooled to room temperature. After removing the potassium carbonate by filtration, the solvent was removed by rotary evaporation. The crude solid product was dissolved in ethyl acetate (150 mL) and then washed thrice with 50 mL of deionized water to collect the organic layer. The organic layer was dried over sodium sulfate and vacuum filtered to remove sodium sulfate. Then the solvent was evaporated, and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to obtain a primrose yellow solid (1.72 g, 7.9 mmol, 61.9%). ^{1}H NMR spectrum of B2-2 was shown in **Figure S2**. ^{1}H NMR (CDCl$_3$, 300 MHz), δ ppm: 6.83 (s, 4H), 5.97-5.83 (m, 2H), 5.19-5.03 (m, 4H), 3.99-3.94 (t, 4H), 2.56-2.48 (m, 4H).

Synthesis of 1,4-bis (pent-4-en-1-yloxy) benzene (B2-3). Under an inert atmosphere, a mixture of hydroquinone (1.1 g, 10.0 mmol), 5-bromo-1-pentene (3.73 g, 25.0 mmol), anhydrous potassium carbonate (6.21 g, 45.0 mmol), and dried acetonitrile (100 mL) was added to a 250 mL three-necked round flask, which was refluxed for 24 h and cooled down to room temperature. After removal of potassium carbonate by filtration, the solvent was removed via rotary evaporation. The crude solid product was dissolved in ethyl acetate (150 mL), which was then wash thrice with 50 mL of deionized water, and the organic layer was collected. The organic layer was dried over sodium sulfate and vacuum filtered to remove sodium sulfate. Then the solvent was evaporated, and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to obtain a white solid (1.02 g, 4.1 mmol, 41.5%). ^{1}H NMR spectrum of B2-3 was shown in **Figure S3**.

^{1}H NMR (CDCl$_3$, 300 MHz), δ ppm: 6.84 (s, 4H), 5.92-5.81 (m, 2H), 5.11-5.00 (m, 4H), 3.96-3.92 (t, 4H), 2.27-2.24 (m, 4H), 1.91-1.86 (m, 4H).

Synthesis of 1,4-bis (hex-5-en-1-yloxy) benzene (B2-4). Under an inert atmosphere, a mixture of hydroquinone (5.5 g, 50.0 mmol), 6-bromo-1-hexene (4.07 g, 125.0 mmol), anhydrous potassium carbonate (31.1 g, 225.0 mmol), and dried acetonitrile (100 mL) was added to a 250 mL three-necked round flask, which was refluxed for 48 h and cooled down to room temperature. After removal of potassium carbonate by filtration, the solvent was removed via rotary evaporation. The crude solid product was dissolved in ethyl acetate (150 mL), which was then washed thrice with 50 mL of deionized water, and the organic layer was collected. The organic layer was dried over sodium sulfate and vacuum filtered to remove sodium sulfate. Then the solvent was evaporated, and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to obtain a white solid (10.78 g, 39.3 mmol, 78.6%). ^{1}H NMR spectrum of B2-4 was shown in **Figure S4**. ^{1}H NMR (CDCl$_3$, 300 MHz), δ ppm: 6.81 (s, 4H), 5.89-5.76 (m, 2H), 5.06-4.94 (m, 4H), 3.93-3.89 (t, 4H), 2.16-2.08 (m, 4H), 1.82-1.73 (m, 4H), 1.61-1.51 (m, 4H).

S2 Polymerization kinetics

Kinetic studies of the START terpolymerization with [B1-1]$_0$/[B2-2]$_0$ = 1/1. A typical polymerization procedure is as follows: A mixture of monomers (A, B1-1 and B2-2), NaI ([A]$_0$/[B1-1]$_0$/[B2-2]$_0$/[NaI]$_0$ = 1/0.5/0.5/9, [A]$_0$ = 0.25 mmol), and acetone (2 mL) was prepared in a clean 5 mL ampoule with a stir bar. The mixture was deoxygenated by four freeze-pump-thaw cycles under N$_2$ atmosphere, and the ampoule was immediately sealed by flame. Then, the mixture was stirred under irradiation with purple light LED light (λ$_{max}$ = 403 nm, 29.7 mW cm^{-2}) while cooled with 10 ^{o}C circulating water and an electric fan to maintain room temperature. At the desired exposure time 4, 5, 7, 10, 15, 21, and 34 h, the obtained products were analyzed by ^{1}H NMR and GPC.

Kinetic studies of the START terpolymerization with [B1-1]$_0$/[B2-2]$_0$ = 2/1. A typical polymerization procedure is as follows: A mixture of monomers (A, B1-1 and B2-2), NaI ([A]$_0$/[B1-1]$_0$/[B2-2]$_0$/[NaI]$_0$ = 1/0.67/0.33/9, [A]$_0$ = 0.25 mmol), and acetone (2 mL) was prepared in a clean 5 mL ampoule with a stir bar. The mixture was deoxygenated by four freeze-pump-thaw cycles under N$_2$ atmosphere, and the ampoule was immediately sealed by flame. Then, the mixture was stirred under irradiation with purple light LED light (λ$_{max}$ = 403 nm, 29.7 mW cm^{-2}) while cooled with 10 ^{o}C circulating water and an electric fan to maintain room temperature. At the desired exposure time of 3, 4, 6, 8, 12 and 16 h, the obtained products were analyzed by ^{1}H NMR and GPC.

Kinetic studies of the START terpolymerization with [B1-1]$_0$/[B2-2]$_0$ = 1/2. A typical polymerization procedure is as follows: A mixture of monomers (A, B1-1 and B2-2), NaI ([A]$_0$/[B1-1]$_0$/[B2-2]$_0$/[NaI]$_0$ = 1/0.33/0.67/9, [A]$_0$ = 0.25 mmol), and acetone (2 mL) was prepared in a clean 5

mL ampoule with a stir bar. The mixture was deoxygenated by four freeze-pump-thaw cycles under N_2 atmosphere, and the ampoule was immediately sealed by flame. Then, the mixture was stirred under irradiation with purple light LED light (λ_{max} = 403 nm, 29.7 mW cm^{-2}) while cooled with 10 °C circulating water and an electric fan to maintain room temperature. At the desired exposure time 5, 6, 8, 12 and 16 h, the obtained products were analyzed by ^{1}H NMR and GPC.

S3 Additional tables and figures

Table S1. Effect of catalysts on START terpolymerization.[a]

Entry	Catalyst	Yield [b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	$M_{n,NMR}$ [d] (g mol^{-1})	Đ [c]	$n_{B1\text{-}1}/n_{B2\text{-}2}$ [e]
1	TMEDA	31.6	8600	5100	1.56	0.98/1
2	Et$_3$N	62.8	8600	10300	1.49	0.89/1
3	DMBA	73.8	8700	9900	1.45	0.96/1
4	TBAI	33.2	4300	3900	1.15	0.97/1
5	NaI	32.1	3800	3500	1.13	0.92/1

[a]Feed molar ratio R = [A]$_0$/[B1-1]$_0$/[B2-2]$_0$/[Catalyst]$_0$ = 1/0.5/0.5/0.4, time = 23 h. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. [e]Calculated molar ratio in polymers determined by ^{1}H NMR results.

Table S2. Effect of dose of NaI on START terpolymerization.[a]

Entry	X	Yield [b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	$M_{n,NMR}$ [d] (g mol^{-1})	Đ [c]	n_{B1-1}/n_{B2-2} [e]
1	0	0	--[f]	--[f]	--[f]	--[f]
2	0.4	32.1	3800	3500	1.13	0.92/1
3	2.0	34.3	4400	4300	1.17	0.88/1
4	5.0	42.1	4500	4300	1.18	0.92/1
5	9.0	55.7	5100	5300	1.25	1.02/1
6	12.0	56.6	5400	5700	1.29	0.97/1

[a]Feed molar ratio R = $[A]_0/[B1-1]_0/[B2-2]_0/[NaI]_0$ = 1/0.5/0.5/X, time = 23 h. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. [e]Calculated molar ratio in polymers determined by ^{1}H NMR results. [f]Not available.

Table S3. Experimental results of binary polymerization by START. [a]

Entry	A/B	Yield [b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	$M_{n,NMR}$ [d] (g mol^{-1})	Đ [c]
S1	A/B1-1	58.6	5600	6600	2.50
S2	A/B2-2	71.5	6100	5000	2.14
S3	A/B2-3	70.4	5800	3000	3.12
S4	A/B2-4	56.6	5700	4600	2.29

[a]Feed molar ratio R = $[A]_0/[B]_0/[NaI]_0$ = 1/1/9, time = 23 h. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. The GPC curves are shown in Figure S17.

Table S4. The Gibbs free energy of chemical reactions (1)-(8) by $\Delta G = G_p - \Sigma G_m$.

Chemical reaction	ΔG/kJ mol^{-1}	Chemical reaction	ΔG/kJ mol^{-1}
(1)	[a]---	(5)	-124.86
(2)	-117.32	(6)	-96.37
(3)	-109.36	(7)	[a]---
(4)	-86.31	(8)	-107.26

The G_p, G_m calculation was performed using Gaussian 16. For the chemical reactions (1)-(8), the C, H, O, and F atoms were treated with the split-valence 6-31G(d,p) basis set, while the I atom was described by the Stuttgart effective core potential. [a]not available.

Table S5. Kinetic studies of the START terpolymerization with $[B1-1]_0/[B2-2]_0 = 1/1$.[a]

Entry	Time (h)	Yield[b] (%)	$M_{n,GPC}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	Đ[c]	n_{B1-1}/n_{B2-2}[e]
1	4	8.6	3000	3400	1.13	1.00/1
2	5	14.3	3000	3100	1.15	1.10/1
3	7	20.8	4300	4600	1.21	0.96/1
4	10	41.2	4700	4800	1.30	1.02/1
5	15	52.0	5200	5300	1.36	1.03/1
6	21	55.7	5300	4700	1.31	1.08/1
7	34	65.9	6100	5800	1.29	1.03/1

[a]Feed molar ratio R = $[A]_0/[B1-1]_0/[B2-2]_0/[NaI]_0$ = 1/0.5/0.5/9. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. [e]Calculated molar ratio in polymers determined by ^{1}H NMR results.

Table S6. Kinetic studies of the START terpolymerization with $[B1\text{-}1]_0/[B2\text{-}2]_0 = 2/1$.[a]

Entry	Time (h)	Yield [b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	$M_{n,NMR}$ [d] (g mol^{-1})	$Đ$ [c]	$n_{B1\text{-}1}/n_{B2\text{-}2}$ [e]
1	3	13.8	3600	3900	1.14	1.29/1
2	4	22.8	3700	3800	1.14	1.46/1
3	6	30.3	4100	3900	1.15	1.61/1
4	8	36.4	4200	4600	1.15	1.84/1
5	12	44.9	4300	4900	1.19	2.01/1
6	16	55.6	5400	5500	1.26	2.00/1

[a]Feed molar ratio R = $[A]_0/[B1\text{-}1]_0/[B2\text{-}2]_0/[NaI]_0$ = 1/0.67/0.33/9. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. [e]Calculated molar ratio in polymers determined by ^{1}H NMR results.

Table S7. Kinetic studies of the START terpolymerization with $[B1\text{-}1]_0/[B2\text{-}2]_0 = 1/2$.[a]

Entry	Time (h)	Yield [b] (%)	$M_{n,GPC}$ [c] (g mol^{-1})	$M_{n,NMR}$ [d] (g mol^{-1})	$Đ$ [c]	$n_{B1\text{-}1}/n_{B2\text{-}2}$ [e]
1	5	15.0	3300	3000	1.14	1/1.48
2	6	20.3	3900	3800	1.14	1/1.60
3	8	35.1	4100	3700	1.24	1/1.82
4	12	48.5	4300	3900	1.26	1/2.01
5	16	53.5	4800	4500	1.24	1/2.00

[a]Feed molar ratio R = $[A]_0/[B1\text{-}1]_0/[B2\text{-}2]_0/[NaI]_0$ = 1/0.33/0.67/9. [b]Determined by gravimetry. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by ^{1}H NMR results. [e]Calculated molar ratio in polymers determined by ^{1}H NMR results.

Table S8. Glass transition temperature (T_g) of alternating terpolymers.[a]

Entry	B1-1/B2-2	n_{B1-1}/n_{B2-2}[b]	$M_{n,GPC}$[c] (g mol^{-1})	$Đ$[c]	T_g[d] (°C)
1		1/0.55	5500	1.35	11
2	1/0.5	1/0.53	4100	1.26	11
3		1/0.42	5400	1.56	9
4		1/0.93	5300	1.31	17
5	1/1	1/0.96	5800	1.37	15
6		1/1.12	4300	1.24	16
7		1/1.75	5200	1.37	22
8	1/2	1/1.79	4800	1.20	24
9		1/1.96	4600	1.36	22

[a]Feed molar ratio R = [A]$_0$/[B1-1+B2-2]$_0$/[NaI]$_0$ = 1/1/9, time = 23 h. [b]Calculated molar ratio in polymers determined by ^{1}H NMR results. [c]Determined by GPC using PMMA as the standard in THF. [d]Determined by DSC.
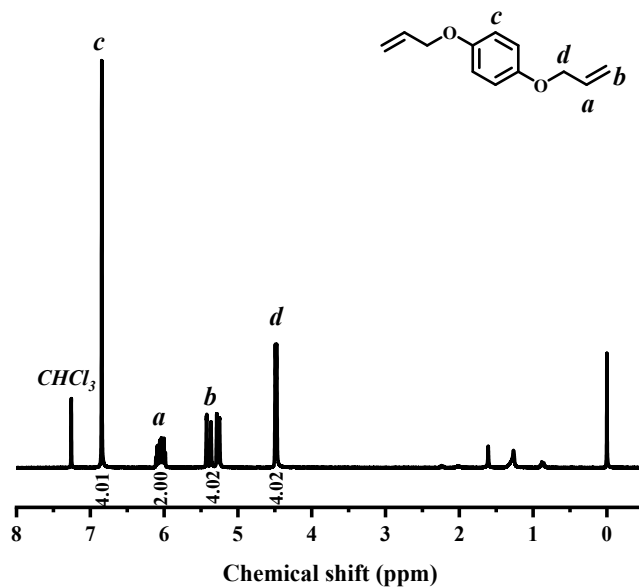
Figure S1. ^{1}H NMR spectrum of **B2-1** in CDCl$_3$.
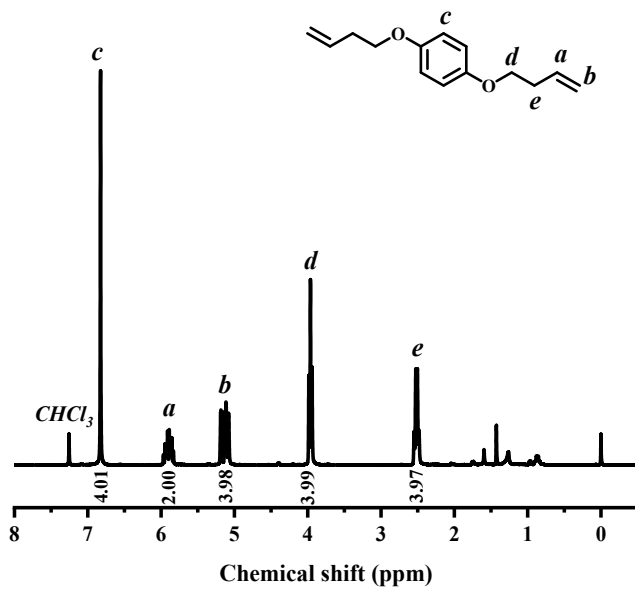
Figure S2. ^{1}H NMR spectrum of **B2-2** in CDCl$_3$.
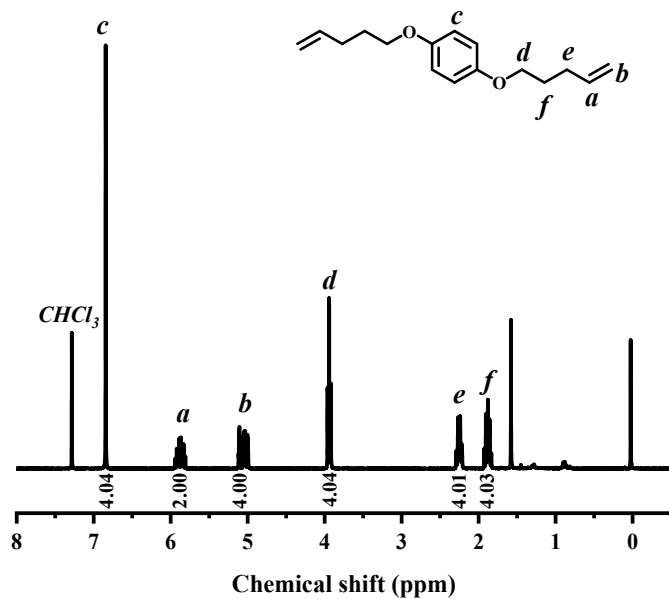
Figure S3. ^{1}H NMR spectrum of **B2-3** in CDCl$_3$.
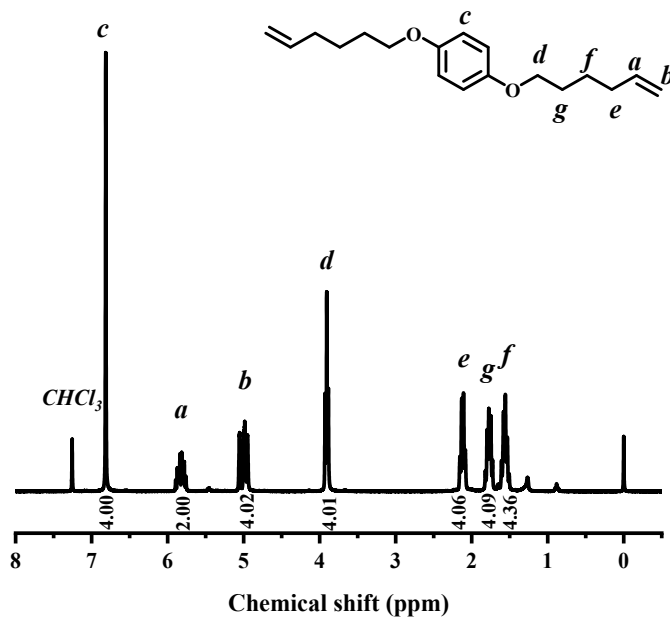
Figure S4. ^{1}H NMR spectrum of **B2-4** in CDCl$_3$.
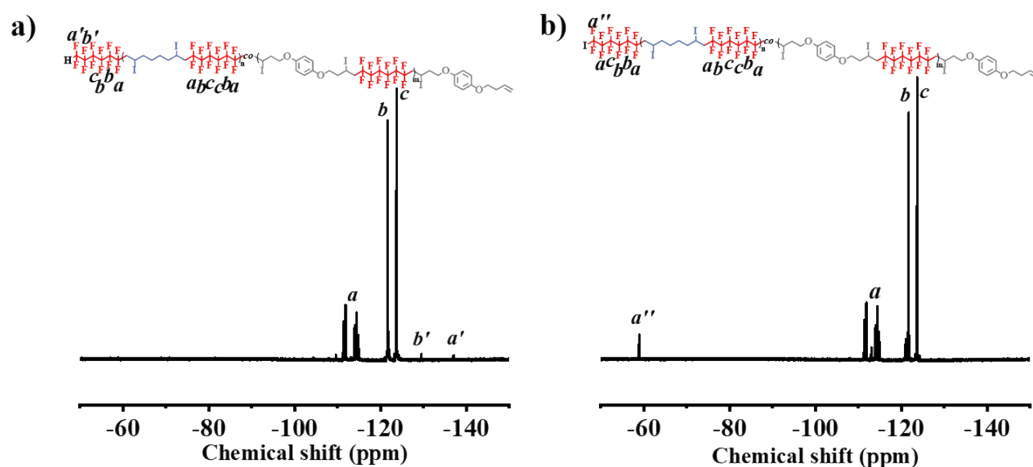
Figure S5. ^{19}F NMR spectra of SFATs by using a) DMBA and b) NaI as the catalysts in CDCl$_3$.
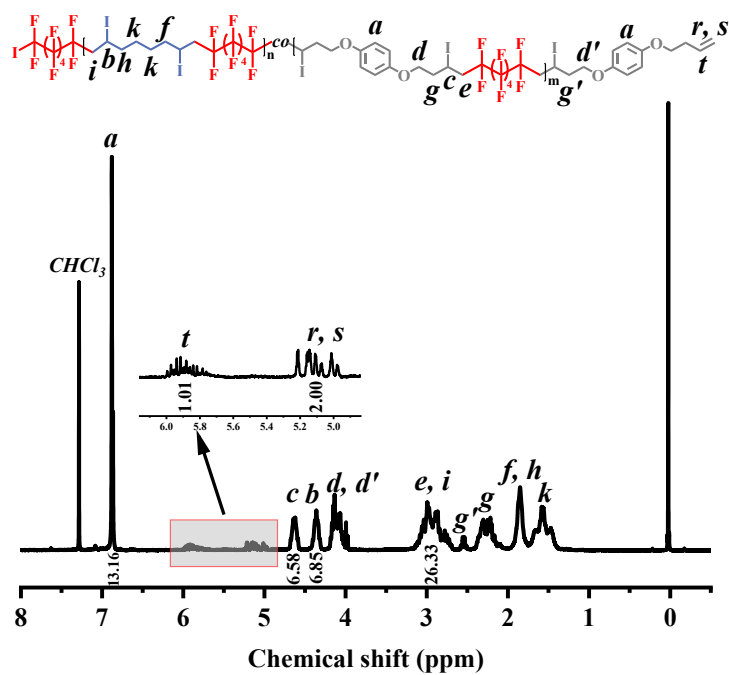
Figure S6. ^{1}H NMR spectrum of SFAT-3 shown in Table 1.
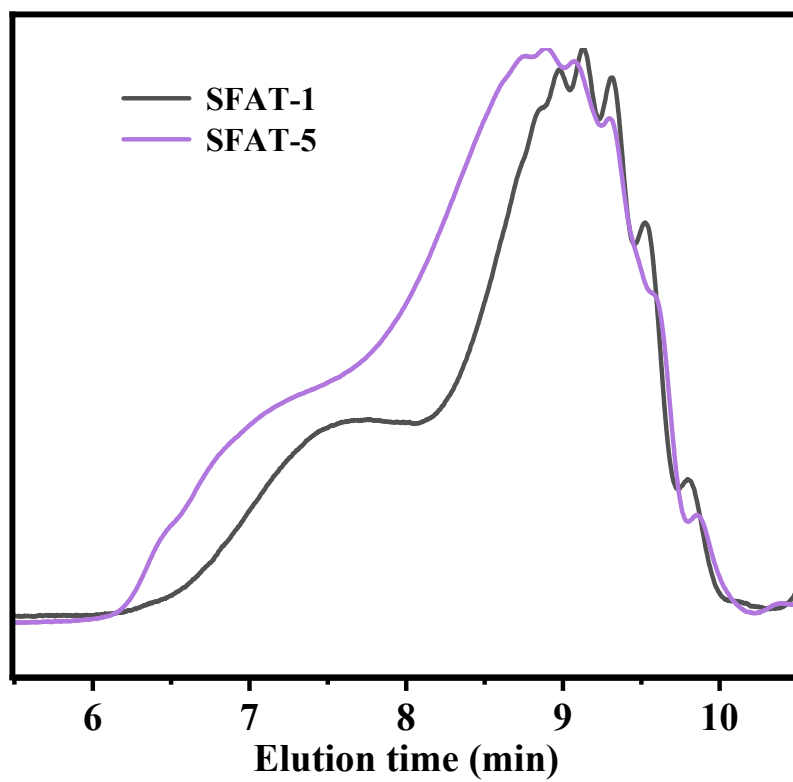
Figure S7. GPC curves of SFAT-1 and SFAT-5 shown in Table 1.
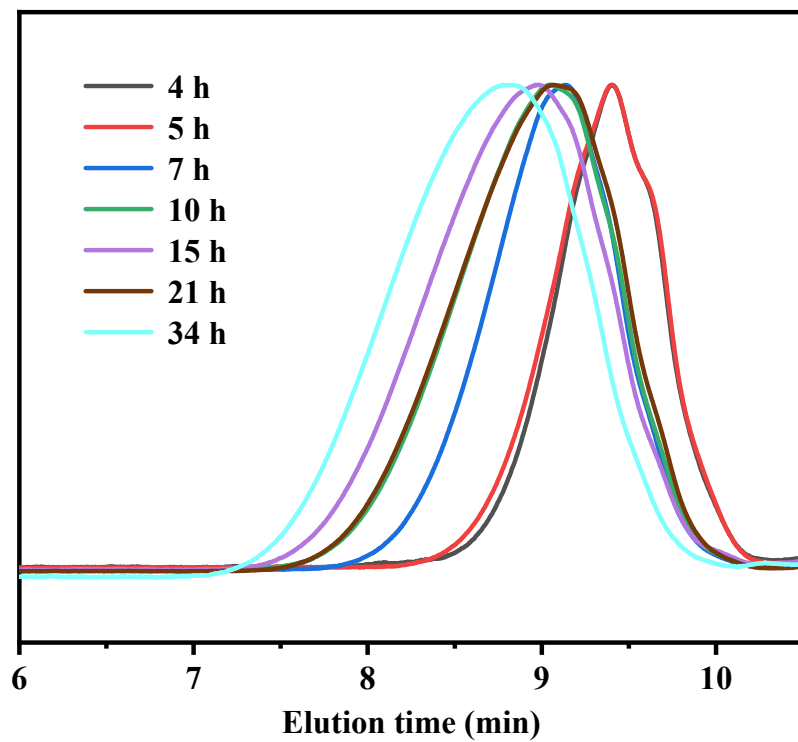
Figure S8. GPC curves of terpolymers obtained at $[B1\text{-}1]_0/[B2\text{-}2]_0 = 1/1$ during the kinetic investigation.
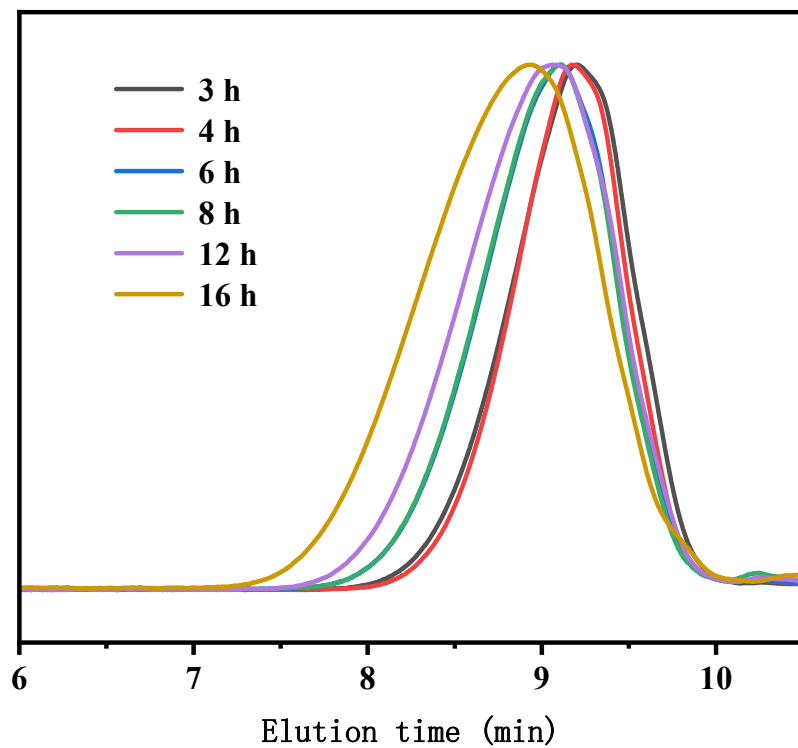
Figure S9. GPC curves of terpolymers obtained at $[B1\text{-}1]_0/[B2\text{-}2]_0 = 2/1$ during the kinetic investigation.
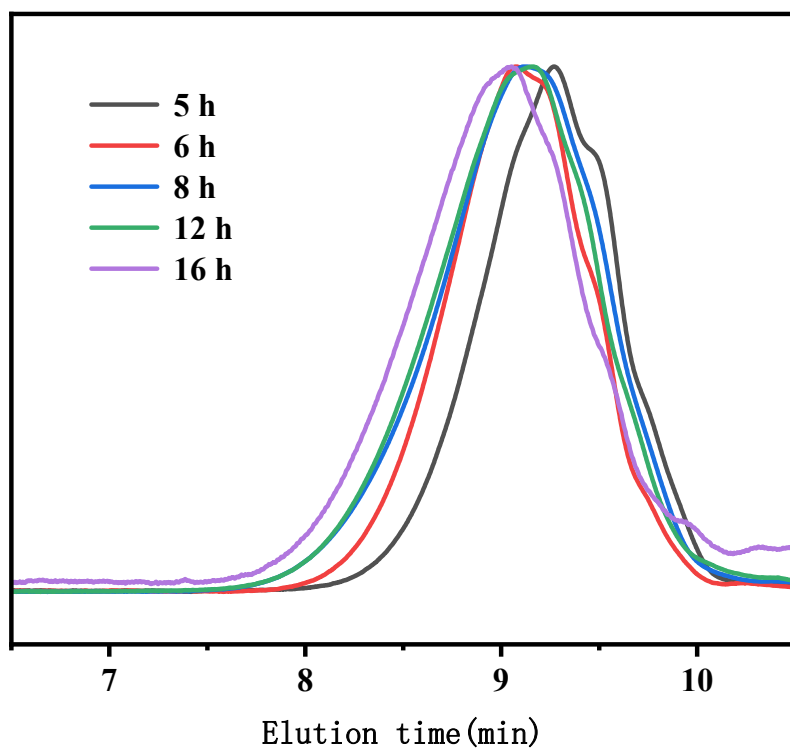
Figure S10. GPC curves of terpolymers obtained at $[B1\text{-}1]_0/[B2\text{-}2]_0 = 1/2$ during the kinetic investigation.
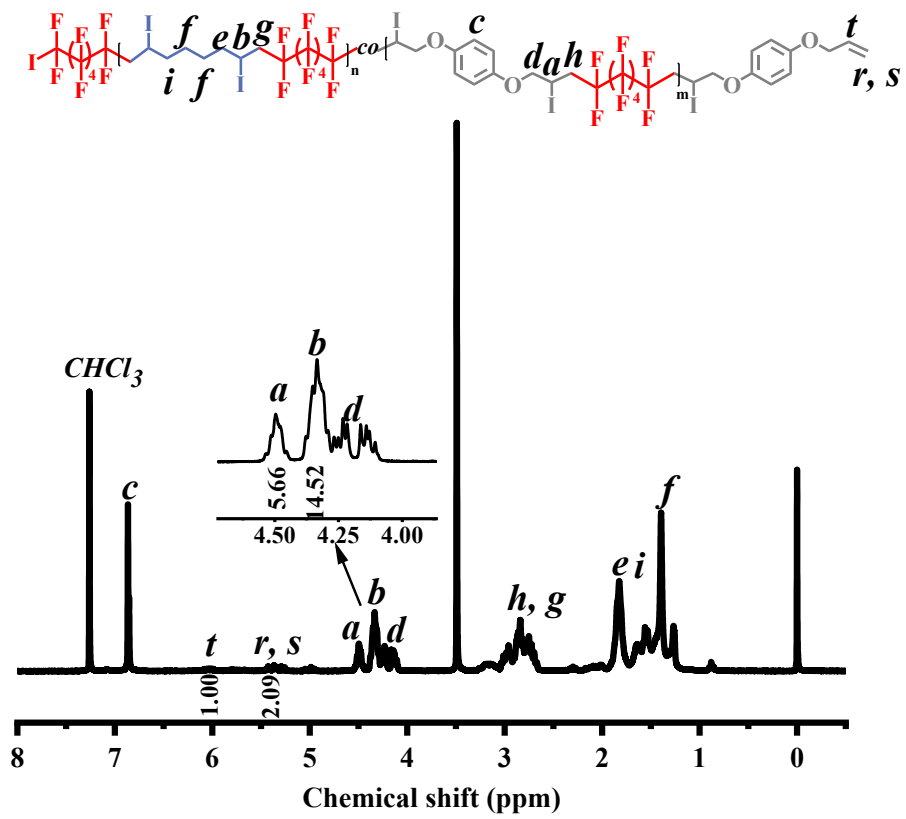
Figure S11. ^{1}H NMR spectra of $(AB1\text{-}1)_{7.3}$-co-$(AB2\text{-}1)_{3.3}$ shown in Table 2.
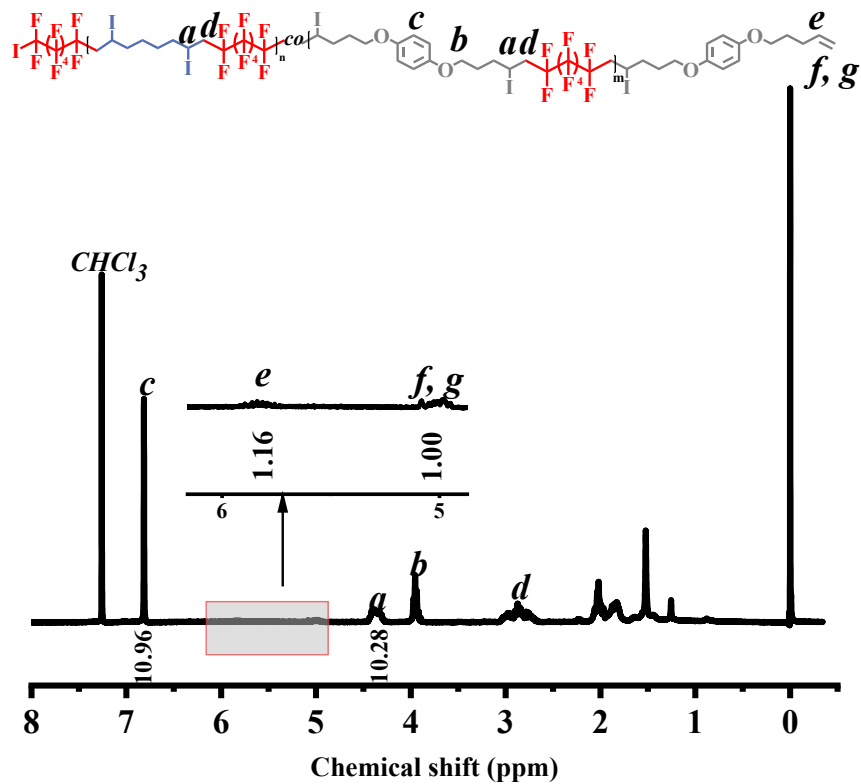
Figure S12. ^{1}H NMR spectra of (AB1-1)$_{3.0}$-*co*-(AB2-3)$_{3.2}$ shown in Table 2.
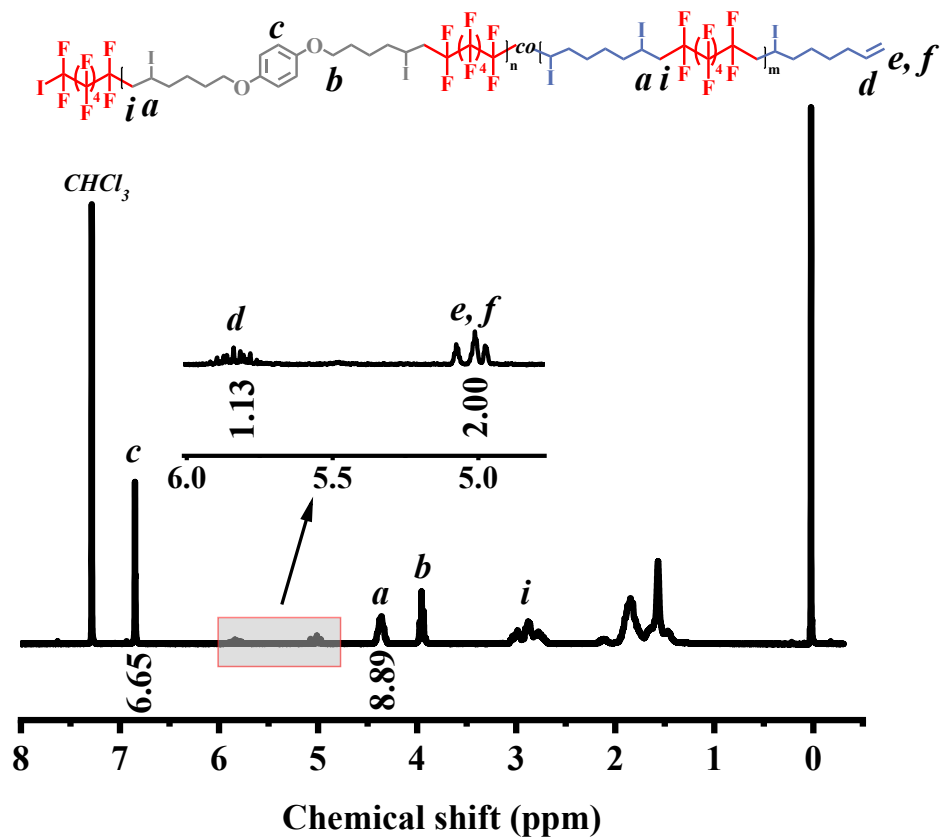
Figure S13. ¹H NMR spectra of (AB1-1)$_{3.3}$-*co*-(AB2-4)$_{2.8}$ shown in Table 2.
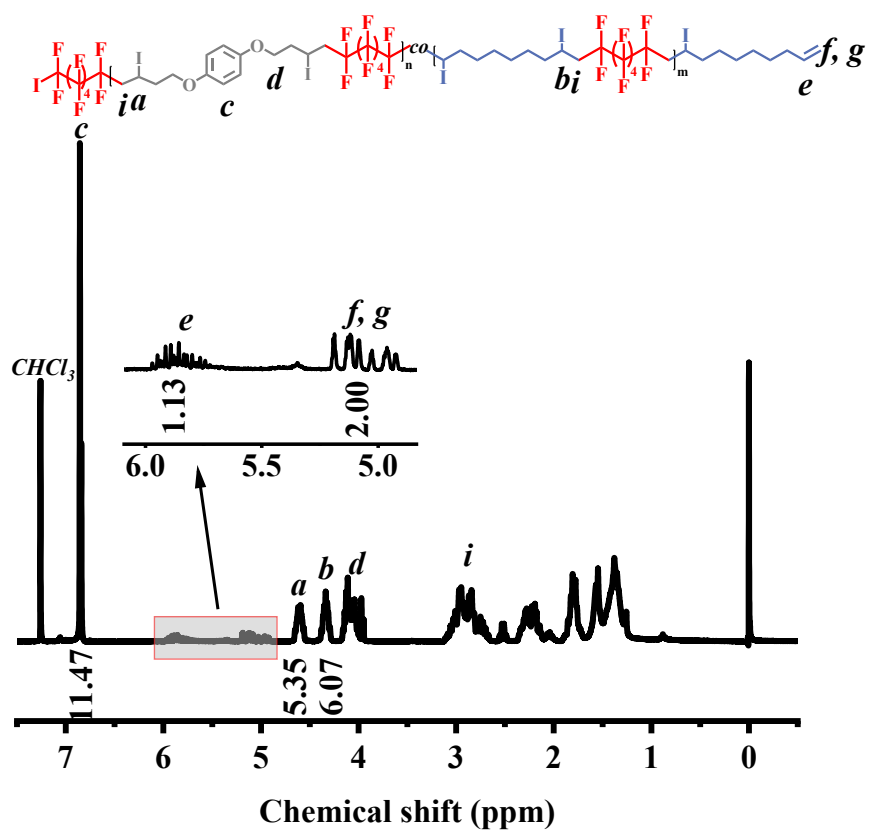
Figure S14. ^{1}H NMR spectra of $(AB1\text{-}2)_{3.5}\text{-}co\text{-}(AB2\text{-}2)_{3.2}$ shown in Table 2.
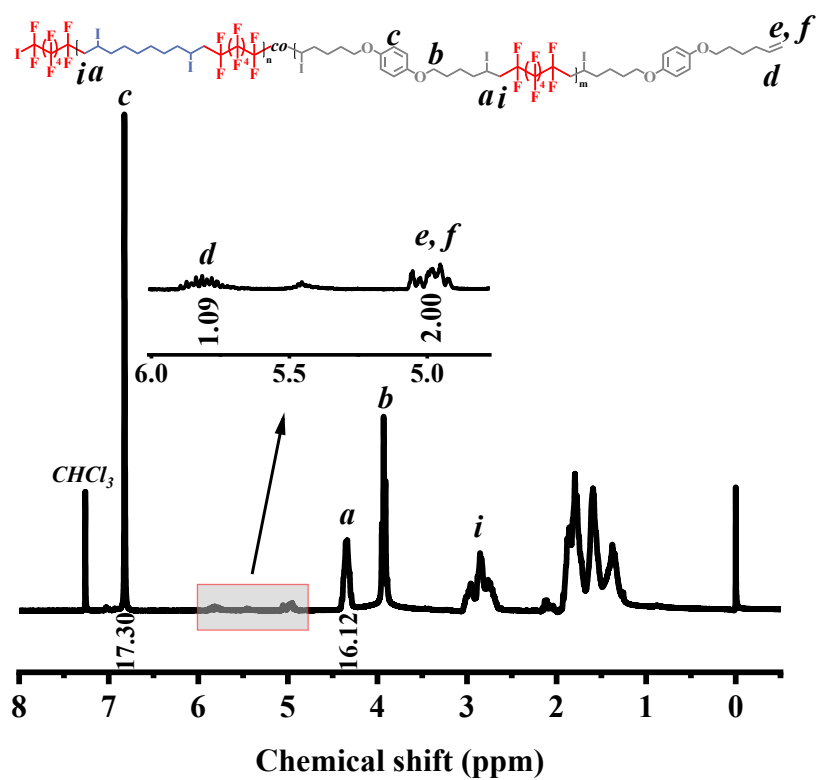
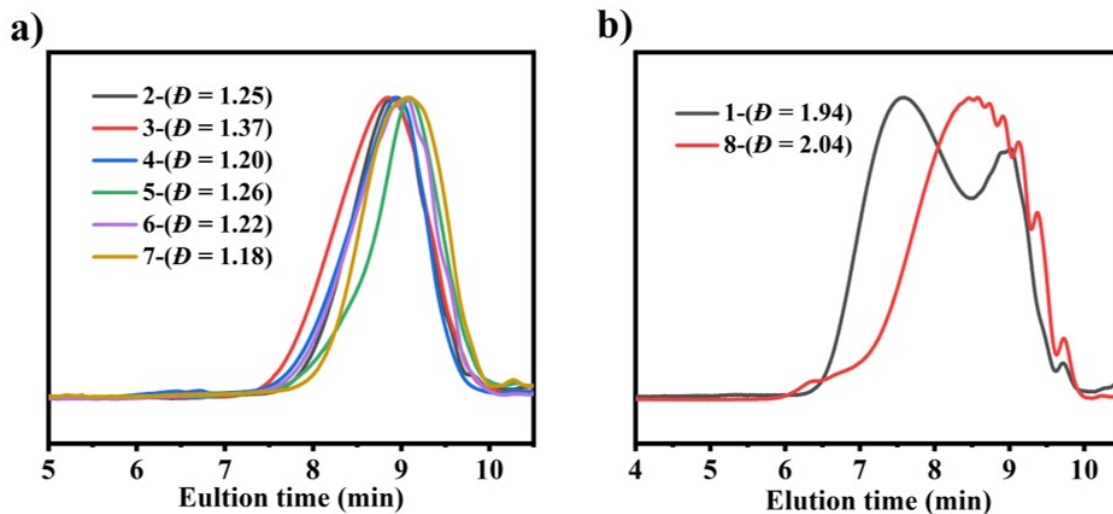**Figure S15**. ^1H NMR spectra of $(AB1\text{-}2)_{4.2}\text{-}co\text{-}(AB2\text{-}4)_{4.8}$ shown in Table 2.

Figure S16. GPC curves of terpolymers of a) entries 2-7 and (b) entries 1 and 8 shown in Table 2.
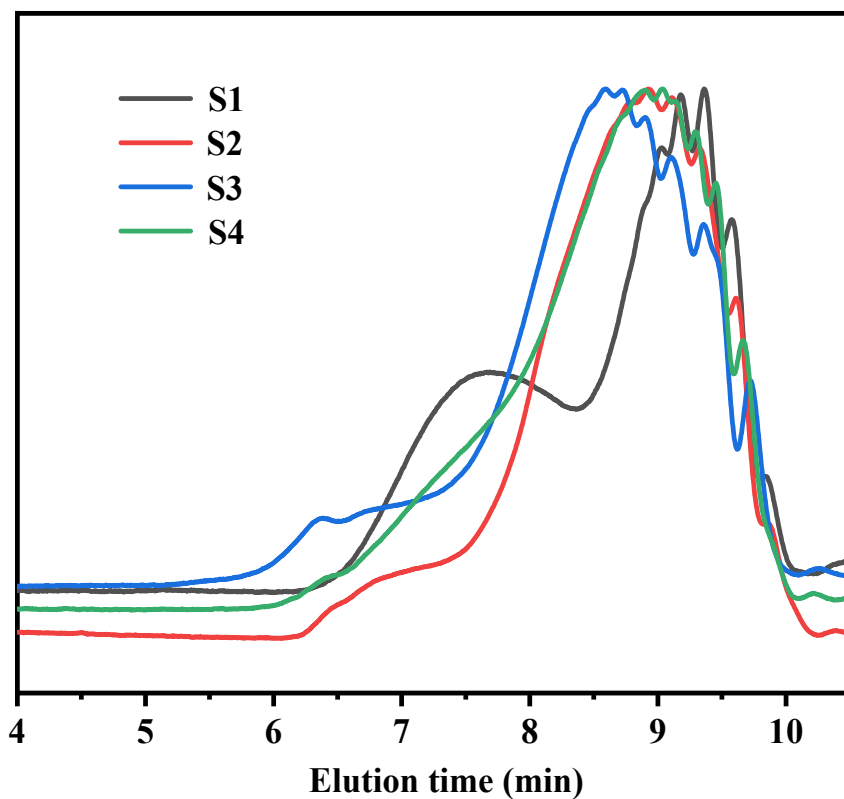

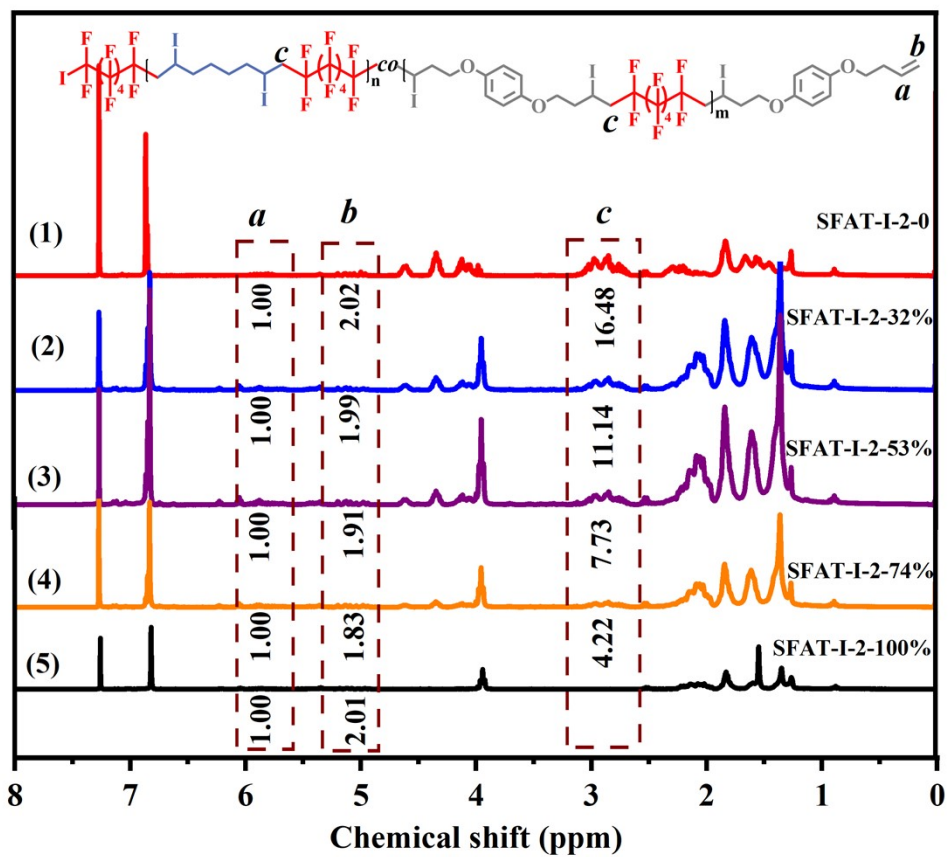**Figure S17**. GPC curves of bipolymers S1-S4 shown in Table S3.

Figure S18. ^{1}H NMR spectra of (1) SFAT-I-2-0, (2) SFAT-I-2-32%, (3) SFAT-I-2-53%, (4) SFAT-I-2-74% and (5) SFAT-I-2-100%.

S4 References

(1) Chen, W.; Mohy Ei Dine, T.; Vincent, S. P. Synthesis of functionalized copillar[4+1]arenes and rotaxane as heteromultivalent scaffolds. *Chem. Commun.* **2021**, *57*, 492-495.

(2) Takeuchi, Y.; Suzuki, Y.; Ono, F.; Manabe, K. Synthesis of 5,5,6,6,21,21,22,22-octamethyl - 5,6,21,22-tetragerma [10.10] paracyclophane. *J. Organomet. Chem.* **2003**, *678*, 61-67.